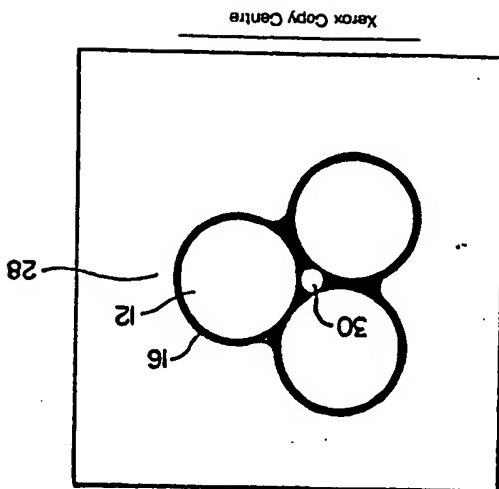


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FIG-4

(57) The present invention provides a ceramic composite (28) having an open porous network and a controlled pore size comprising a plurality of ceramic particles (12) having a fused glass coating (16) and a method for producing the same. The ceramic particles (12) are enveloped by and bonded to adjacent ceramic particles (12) at their interfaces by the glass coating (16). Pores (30) form in the ceramic material (28)

(54) Controlled pore size ceramics particularly for orthopaedic and dental applications.

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# CONTROLLED PORE SIZE CERAMICS PARTICULARLY FOR ORTHOPAEDIC AND DENTAL APPLICATIONS

The present invention relates to a ceramic having a controlled pore size and, more particularly, to a controlled pore structure, liquid phase sintered ceramics for orthopaedic and dental applications.

Ceramic materials which are useful as bone substitutes are used in numerous orthopaedic and dental applications including as implants. Examples of such bone

substitutes are described in U.S. Patent Nos. 4,097,935 to Jarcho; 4,113,500 to Ebihara et al; 4,149,893 to Aoki et al; and 4,330,514 to Nagai et al.

Two bone substitute materials, hydroxyapatite and tricalcium phosphate, have been approved for general dental implant use, and in some selected instances, orthopaedic

clinical trials. However, these materials are only available in particulate or solid bulk closed cell forms. Thus, the use of such materials in orthopaedic and dental applications has been limited.

Bone substitutes such as hydroxyapatite have been combined with other agents in various medical applications. Surgical cements including hydroxyapatite as the bone substitute are used in numerous orthopaedic and dental applications including repairing bone fractures, in attaching bone plates and other prostheses, in bridging comminuted fractures, and in filling or aligning dental cavities. Examples of such compositions are described in U.S. Patent Nos. 4,518,430 to Brown et al; and 4,542,167 to Aoki et al. U.S. Patent No. 4,451,235 to Okuda et al discloses a dental root material comprising hydroxyapatite and an organic matrix such as polyethylene.

U.S. Patent No. 4,135,935 to Pfeil et al discloses a composite material useful as an implant. A first starting material which is preferably an apatite and a second starting material which is preferably a glass are ground, preferably jointly, to a particle size preferably between about 200-500 microns. The resultant mixture is finely comminuted to a particle size preferably between about 20-50 microns. The mixture is compressed to form shaped bodies and sintered. This material does not have the open pore structure which characterizes the ceramic material of the present invention.

The present invention provides a ceramic composite having an open porous network of controlled pore size comprising a plurality of ceramic particles having a glass coating which bonds the ceramic particles at their interfaces. While the present invention is particularly directed to providing ceramics which are useful in orthopaedic and surgical applications, those skilled in the art will appreciate that the teachings herein are relevant to ceramics generally where a controlled pore size is desired. By varying the size of the ceramic particles and the thickness of the glass coating, the pore size of the composite ceramic can be varied.

According to one aspect of the present invention, ceramic particles have a coating of a fused glass on the surface thereof.

Accordingly, one object of the present invention is to provide a ceramic material having a controlled pore size.

5 A further object of the present invention is to provide a ceramic composite having a controlled pore size comprising a plurality of particles of a bone ingrowth promoting material useful in dental and orthopaedic applications.

10 An additional object of the present invention is to provide a ceramic composite having a controlled pore size useful in dental and orthopaedic applications wherein the degree of resorbability can be varied.

Another object of the present invention is to provide ceramic particles having a finely divided or fused glass coating useful in providing a ceramic composite

15 having a controlled pore size. Still another object of the present invention is to provide a process for preparing a ceramic composite in accordance with the present invention.

20 Other objects and advantages of the present invention will become apparent from the following description and the appended claims.

In order that the invention may be more readily understood, reference will now be made to the accompanying drawings, in which:

25 Figure 1 illustrates an agglomerator useful in coating the ceramic particles of the present invention with a ground glass.

30 Figure 2 illustrates a spray dryer useful in coating the ceramic particles of the present invention with a ground glass.

Figure 3 illustrates the ceramic particles of the present invention with a glass powder coating prior to sintering.

Figure 4 illustrates a plurality of the ceramic particles of the present invention with a glass coating after liquid phase sintering.

Figure 5 is a scanning electron microscope photograph (magnification 50X) of a ceramic in accordance with the present invention showing the glass coated ceramic particles and the glass necking between them.

Figure 6 illustrates a prosthesis carrying ceramic particles in accordance with the present invention. As stated earlier, the principal object of the present invention is to provide a ceramic composite having a controlled pore size. In order to achieve this object, the size of the ceramic particles must be controlled. Knowing the size of the ceramic particle and the thickness of the glass coating, the pore size of the ceramic material can be calculated by using the equation for closely packed particles. The ceramic particles used in the present invention typically have a particle size of less than about 2000 microns. If the particle size is larger than 2000 microns, the present invention can be used, but usually there are more expedient means available to achieve the desired pore size. The amount of glass necking is also less and the porous ceramic is not as strong. Preferably, the ceramic particles of the present invention have a size of about 100 to 1000 microns and, more preferably 500 to 1000 microns.

The ceramic composite of the present invention has broad application because the ceramic particles can

be any of a variety of ceramic materials. It is useful in providing bone implants, surgical cements or grouts, and drug delivery devices. Outside of the biomedical field its open cell pore structure is useful in providing microporous filters.

Typical examples of useful ceramics are  $Al_2O_3$ ,  $MgO$ ,  $ZrO_2$ ,  $SiC$ , etc. However, the ceramic composite of the present invention is particularly useful in dental and orthopaedic applications. Ceramic particles which are useful for such dental and orthopaedic applications are a

bone ingrowth promoting material. The term "bone ingrowth promoting material" means a material, which upon implanting into the human body, will promote or aid the growth of new bone around the ceramic material. This material may function as a scaffold for bone growth and/or provide nutrients which promote bone growth.

In some applications, it is anticipated that a ceramic particle of a nonresorbable bone ingrowth promoting material would be useful. Examples of nonresorbable bone ingrowth promoting materials are hydroxyapatite, aluminum oxide, pyrolytic carbon, etc. A preferred nonresorbable bone ingrowth promoting material is hydroxyapatite.

Examples of commercially available hydroxyapatite include Calcitite 2040, a nonresorbable synthetic hydroxyapatite. Examples of available hydroxyapatite are produced by Bior Products, Inc. of San Diego, California, and by the Lab of Richmond, California.

In other applications, the ceramic particles are a resorbable bone ingrowth promoting material. Examples of useful resorbable bone ingrowth promoting materials

- include various calcium aluminates, calcium phosphates, calcium aluminophosphates and calcium sulfates. A preferred resorbable bone ingrowth promoting material is tricalcium phosphate. Specific examples of resorbable bone ingrowth promoting materials are the ALCAP (calcium aluminophosphate) ceramic described in U.S. Patent No. 4,218,255 to Bajpai in ground or powdered form; calcium phosphates described in U.S. Patent No. 4,192,021; and the ALCAP ceramics described by Graves, G. A., et al, "Resorbable Ceramic Implants," J. Biomed. Mater. Res. Symp. 2 (Part I): 91, 1972.
- Calcium aluminophosphate ceramics useful in the present invention can be obtained by mixing calcium oxide ( $\text{CaO}$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ), and phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) in weight ratios of about 35 to 40%  $\text{CaO}$ , about 45 to 55%  $\text{Al}_2\text{O}_3$ , and about 10 to 20%  $\text{P}_2\text{O}_5$ ; comprising the mixture; and calcining. A typical ceramic is prepared from a 38:50:12 mixture of calcium oxide, aluminum oxide, and phosphorus pentoxide which is calcined at 1300°C for 12 hours and ground.
- Resorbable and nonresorbable bone ingrowth promoting materials may be combined to provide a partially resorbable ceramic. For example, in order to stimulate bone growth, it may be desirable to formulate the composition such that a major or a minor portion of the ceramic is resorbed.
- The ceramic particles of the present invention are enveloped by a fusible glass and are bonded to adjacent ceramic particles at their interfaces by the fusible glass. Any glass is useful in the ceramic material of the present

invention, but preferably, a biocompatible glass having a melting point in the range of about 500 to 1000°C is used. In many biological applications, the fusible glass is resorbable. A particularly useful resorbable

5 glass comprises calcium oxide (CaO) and phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>). Other ingredients such as calcium

fluoride (CaF<sub>2</sub>), water (H<sub>2</sub>O), and other metal oxides

containing cations such as magnesium, zinc, strontium, sodium, potassium, lithium, silicon, boron and aluminum

10 oxides may also be incorporated in small amounts. In terms of the binary mixture, the preferred Ca:P mole ratio

ranges from about 0.25 to 0.33. Preferably, the glass

comprises by weight 5-50% CaO, 50-95% P<sub>2</sub>O<sub>5</sub>, 0-5% CaF<sub>2</sub>, 0-5% H<sub>2</sub>O and 0-10% of a metal oxide selected

15 from the group consisting of magnesium, zinc, strontium, sodium, potassium, lithium, and aluminum oxides. In a

preferred embodiment, the calcium oxide (CaO) is present

by weight in the amount of 15-25%; the phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) is present by weight in the amount of 65-90%

20 while either calcium fluoride (CaF<sub>2</sub>) or water (H<sub>2</sub>O) is present by weight in the amount of 0.1-4%.

comparable to the ceramic particles, the degree of resorbability of the glass coating can be controlled.

25 For example, as the amount of CaO increases, the degree of resorbability decreases. Also, as the amount of Na<sub>2</sub>O increases, the degree of resorbability decreases. Additions of potassium, aluminum or zinc oxide can also be

made to achieve varying degrees of resorption in body fluids. The glass compositions can be formulated to have

30 a range of solubility rates or be virtually insoluble.



10 In making the ceramic material of the present invention, the glass is ground to a particle size of about 10 to 50 microns and coated on the surface of the larger ceramic particles. The particle size should be as uniform as possible.

15 Typically the glass is adhered to the ceramic particles as a slurry in a solution of a binder such as polyvinyl alcohol (PVA). When the ceramic is subsequently sintered, the binder burns off. The coating is typically about the thickness of the glass particle, although thicker coatings may also be useful. The weight ratio of the ceramic particles to the glass coating is about 8:1 to 14:1 and preferably about 10:1 to 12:1. In a preferred embodiment, the ratio which provides a desirable thin coating with good porosity and good necking between the ceramic particles is about 11:1. Of course, this will vary with the particle size of the ceramic.

Example	CaO	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	MgO	ZnO	SiO <sub>2</sub>
A	10	--	--	12	--	1	3	74
B	--	58	--	37	5	--	--	--
C	--	56	21	20	--	--	3.0	--
D	--	63	--	30	7	--	--	--
E	20	80	--	--	--	--	--	--

TABLE 1

In Table 1 below, glass compositions are provided in order of increasing resorbability:

Methods for obtaining hydroxyapatite and tricalcium phosphate particles are known in the art. Two relatively new techniques can also be used. One is sol-gel processing, a method of preparing solid materials that result when certain combinations of chemicals are mixed and precipitated from solution. The sol-gel, if dried slowly, can yield very fine grained ceramics which sinter to high density. The second is a process that provides particles of well controlled size and shape by using spray drying and agglomeration techniques which, until now, were used primarily in the food and drug industry. A slurry of the ceramic and a binder such as PVA is fed to a spray dryer (e.g., a Bowen Ceramic Spray Dryer, Bowen Engineering, Inc. Somerville, N.J.) where it is atomized into fine droplets which are rapidly dried to yield relatively uniform spheres of the ceramic which are sintered for example in a tunnel kiln. Both techniques after sintering provide dense, spherical shaped ceramic particles such as hydroxyapatite or tricalcium phosphate in controlled sizes which may be used to form the porous ceramic of the invention. These materials are also available commercially.

Figure 1 illustrates an agglomerator 10 useful in coating the ceramic particles of the present invention with glass. Ceramic particles 12 are fed by air through tube 14 into the agglomerator 10. A slurry of a glass powder 16 in a binder is fed to a rotary disc 18 through tube 17. As the disc 18 rotates, the glass powder 16 collides with and coats ceramic particles 12. The glass coated particles roll off the plate 18 and are dried in a

hot air stream and collected. The resulting glass coated ceramic particles 20 appear as schematically illustrated in Figure 3.

- Figure 2 illustrates a spray dryer 22 useful in coating the ceramic particles 12 with the glass powder slurry 16. Glass powder 16 is fed through a tube 24 into spray dryer 22. The ceramic particles 12 are dropped through tube 26 into the spray dryer 22. The ceramic particles 12 and the glass powder 16 collide and the glass powder 16 coats the ceramic particles 12 to produce the glass coated ceramic particles 20 of Figure 3.
- The glass coated ceramic particles 20 of Figure 3 are lightly compacted into a desired shape and then sintered. The particles may be compacted in a mold under pressures of about 5 to 1000 psi. Virtually any simple shape can be produced. Upon sintering, surface tension causes the glass powder 16 to melt and flow on the surface of the ceramic particles 12 to form the ceramic material 28 of Figure 4. Typically, the glass coated ceramic particles 20 are sintered at temperatures of about 600 to 1200°C (other temperatures can also be used) for about 5 to 30 minutes. The glass powder 16 envelops the ceramic particles 12 and bonds the adjacent ceramic particles 12 at their interfaces by necking between the ceramic particles 12. Pores 30 form in the ceramic material 28. In addition to coating larger ceramic particles with a smaller fusible glass powder, other means are also envisioned for providing glass-coated ceramic particles useful in forming the porous ceramics of the present invention. In particular, ceramic particles such as HA and

- TCP, when formed by spray drying or agglomeration, are sintered prior to coating with glass. This sintering is usually performed by the manufacturer of commercially available materials. However, a continuous process is envisioned in which the sintered particles are fluidized and contacted with the glass powder while they are at an elevated temperature such that the glass films out directly on contact with the surface of the particle.
- To promote bone ingrowth, the ceramic material of the present invention should have, or acquire through resorption, a pore size of at least about 100 microns. Including other applications, the ceramic material has a pore size of about 20 to 150 microns, and preferably, from about 100 to 150 microns.
- In addition to the glass composition and the ceramic particle composition, the glass thickness is a factor in controlling the rate of resorbability of the ceramic composite. In general, for a slowly resorbable ceramic composite, the glass coating is thicker than for a faster resorbable ceramic composite.
- As an example of a completely nonresorbable ceramic composite, hydroxyapatite particles can be coated with an insoluble glass such as Example A in Table I (a typical soda lime glass). If one then wanted to increase the resorbability of the completely nonresorbable ceramic composite, resorbable ceramic particles can be mixed with the hydroxyapatite or a resorbable glass can be used. An example of a completely resorbable ceramic composite is a tricalcium phosphate ceramic particle coated with a glass comprising  $\text{CaO}$  and  $\text{P}_2\text{O}_5$  in a weight & ratio of about 20:80. Thus, the ceramic composites of the present

invention have broad application because the degree and rate of resorption can be widely varied by carefully choosing the proper combination of ceramic particle composition, glass composition and its thickness.

When selecting a ceramic particle and glass for use in the ceramic composite, the mechanical strength of the implant and the rate of bone ingrowth should be considered. The ceramic pore size greatly influences both. Generally, a ceramic having a small pore size exhibits a high strength but a lower rate of ingrowth compared to a ceramic having a larger pore size. If the ceramic and/or glass is resorbable, the pore size will increase as the ceramic ages.

In particular, it is anticipated that a ceramic will be designed to have high strength initially until a callus has formed around the implant and become fully mineralized. By carefully designing the resorption rate of the glass and/or the ceramic particle, the implant will only be absorbed after the new bone has enough strength. Thus, the resorption rate of the ceramic typically will be less than the rate at which new bone forms.

The ceramic composites of the present invention have numerous uses in orthopaedic and dental applications. The ceramic composite may be supplied in a solid form and cut to the desired size by the practitioner. In another application, ceramic particles coated with glass powder or the fused glass powder are sold to the surgeon who would have his own furnace and mold. The mold is filled with the ceramic particles and the ceramic material in the desired shape is sintered.

In another application, it is anticipated that

the glass coated ceramic particles could be adhered to the surface of a prosthetic device to enhance bone attachment to the device. This is accomplished by first applying a

thin glass coating to the prosthesis, adhering glass coated particles to the prosthesis and then sintering. Figure 6

is an example of a prosthesis 40 used in hip replacements. The shank 42 of the prosthesis is driven into the bone.

By applying glass-coated ceramic particles 44 to the shank, bone growth around the prosthesis and attachment of bone to the prosthesis is promoted.

The present invention is illustrated in more detail by the following non-limiting examples:

#### Example 1

Approximately 2 g of a spherical particulate

hydroxyapatite (HA 500, a product of Orthomatrix, Inc.)

screened to 40 x 60 mesh was placed in a glass dish, 4 to 5 drops of a saturated solution of polyvinyl alcohol was

added to the HA. The HA was coated with the PVA solution by spreading it through the solution with a spatula until

it is well coated (approximately 3 to 5 minutes). The PVA coated HA was dried at 90°C and separated with a spatula.

Glass composition E (Table 1) was ground to 10-40 microns and sprinkled over the PVA coated HA. The mixture was

then vibrated to uniformly coat the HA particles (approximately 1-2 minutes). The glass composition uniformly

adhered to the HA particle surfaces. The glass coated HA particles were placed in a 7/32 inch die on a Clifton

Hydraulic Press. Enough HA was placed in the die to displace the plunger of the die approximately 3/8 inch. 100

5 microliters of the PVA solution was then added to the die and the plunger was replaced and the die vibrated until the PVA solution stopped running out of the die (30-60 seconds). The press was activated and the HA particles were compacted (approximately 500 psi). The compacted cylinder was removed from the die and dried at 90°C for approximately 4 hours. The dried cylinder was sintered at 1000°C for 5 minutes.

#### Example 2

10 Hydroxyapatite was bonded to a prosthesis using the following procedure;

The procedure was evenly coated with a thick

15 slurry of a glass having composition E in Table I using a paint brush. The slurry on the surface of the prosthesis was dried at 90°C and glazed by heating at 1000°C for 5 minutes. Glass coated hydroxyapatite particles were pre-

pared as in Example 1 above and spread on the prosthesis and dried. The prosthesis was then fired at 1000°C for 5 minutes and allowed to cool slowly.

20 Having described the invention in detail and by reference to preferred embodiments thereof, it will be

apparent that modifications and variations are possible without departing from the scope of the invention as

defined in the appended claims.

CLAIMS

1. A ceramic composite (28) having an open porous network of a controlled pore size comprising a plurality of ceramic particles (12) having a coating of a fused glass (16) on their surfaces, said ceramic particles (12) being bonded to adjacent ceramic particles (12) at their interfaces by said fused glass coating (16) to provide an open porous network between said ceramic particles (12).
2. A ceramic composite (28) according to claim 1, characterized in that said ceramic particles (12) are a material selected from the group consisting of  $Al_2O_3$ ,  $MgO$ ,  $ZrO_2$ , and  $SiC$ .
3. A ceramic composite (28) according to claim 1, characterized in that said ceramic composite (28) is useful for dental and orthopaedic implants and said ceramic particles (12) are a bone ingrowth promoting material.
4. A ceramic composite (28) according to claim 3, characterized in that said ceramic particles (12) are a nonresorbable bone ingrowth promoting material.
5. A ceramic composite (28) according to claim 4, characterized in that said nonresorbable bone ingrowth promoting material is selected from the group consisting of hydroxyapatite, aluminum oxide, and pyrolytic carbon.



6. A ceramic composite (28) according to claim 3, characterized in that said ceramic particles (12) are a resorbable bone ingrowth promoting material.
7. A ceramic composite (28) according to claim 6, characterized in that said resorbable bone ingrowth promoting material is selected from the group consisting of calcium aluminate, calcium phosphates, calcium aluminophosphates and calcium sulfates.
8. A ceramic composite (28) according to claim 7, characterized in that said ceramic composite (28) has a pore size of about 20 to 150 microns.
9. A ceramic composite (28) according to claim 8, characterized in that said ceramic composite (28) has a pore size of at least about 100 microns.
10. A ceramic composite (28) according to claim 9, characterized in that said glass (16) is resorbable.
11. A ceramic composite (28) according to claim 10, characterized in that said resorbable glass comprises calcium oxide (CaO) and phosphorus pentoxide ( $P_2O_5$ ).

12. A ceramic composite (28) according to claim 11, characterized in that said resorbable glass comprises by weight:

5	CaO	5-50%
	P <sub>2</sub> O <sub>5</sub>	50-95%
	CaF <sub>2</sub>	0-5%
	H <sub>2</sub> O	0-5%
	XO	0-10%

10 wherein XO is a metal oxide selected from the group consisting of magnesium, zinc, strontium, sodium, potassium, lithium and aluminum oxides.

13. A ceramic composite (28) according to claim 12, characterized in that said ceramic particles (12) have a particle size of less than about 2000 microns.

14. A ceramic composite (28) according to claim 13, characterized in that said ceramic particles (12) have a particle size of about 500 to 1000 microns.

15. A ceramic composite (28) according to claim 14, characterized in that the ratio of said ceramic particles (12) to said glass coating (16) based on the weight of said ceramic composite (28) is about 8:1 to 14:1.

- 5 ceramic particles (20) into a desired shape and sintering.
16. A ceramic composite (28) according to claim 15, characterized in that said ceramic composite (28) is formed by coating said ceramic particles with fusible glass particles (16), molding said fusible glass coated ceramic particles (20) into a desired shape and sintering.
17. A ceramic composite (28) according to claim 16, characterized in that said ceramic particles (12) are coated with said fusible glass particles (16) in an agglomerator (10) or a spray dryer (22).
18. Ceramic particles (12) having a coating of a fused glass (16) on the surface thereof.
19. Ceramic particles (12) according to claim 18, characterized in that said glass (16) comprises calcium oxide (CaO) and phosphorus pentoxide ( $P_2O_5$ ).
20. Ceramic particles (12) according to claim 19, characterized in that said particles (12) are a bone ingrowth promoting material.
21. A process for preparing a ceramic composite (28) having a controlled pore size comprising the steps of: coating ceramic particles (12) with a glass (16), molding said glass coated ceramic particles (20) into a desired shape, and sintering.

22. A process according to claim 21, characterized in that said glass (16) is a fusible glass powder.
23. A process according to claim 22, characterized in that said ceramic particles (12) are coated with said fusible glass particles (16) in an agglomerator (10) or a spray dryer (22).
24. A ceramic composite (28) according to claim 9, characterized in that said glass (16) is non-resorbable.

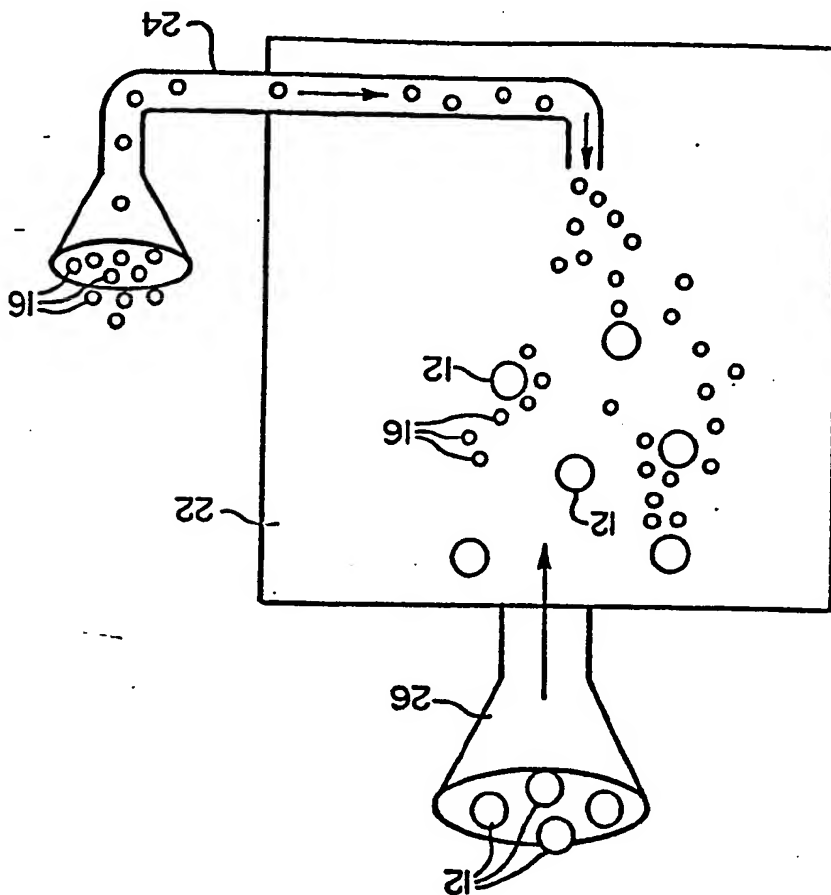


FIG-2

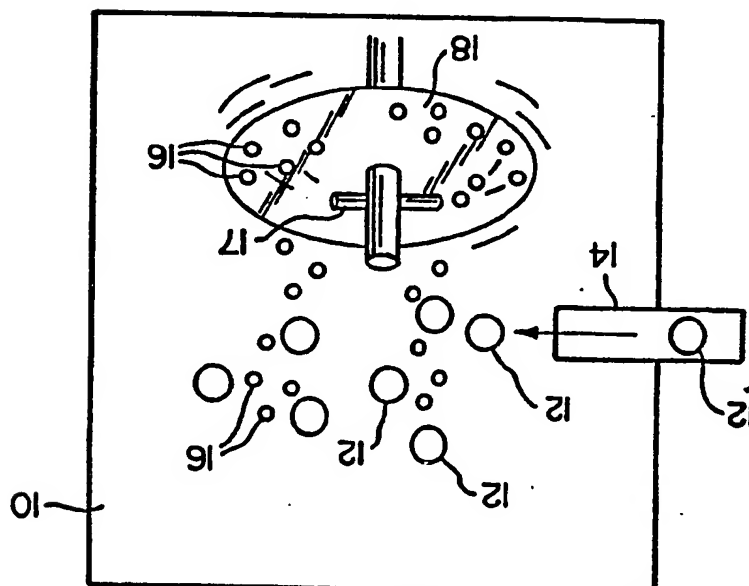


FIG-1

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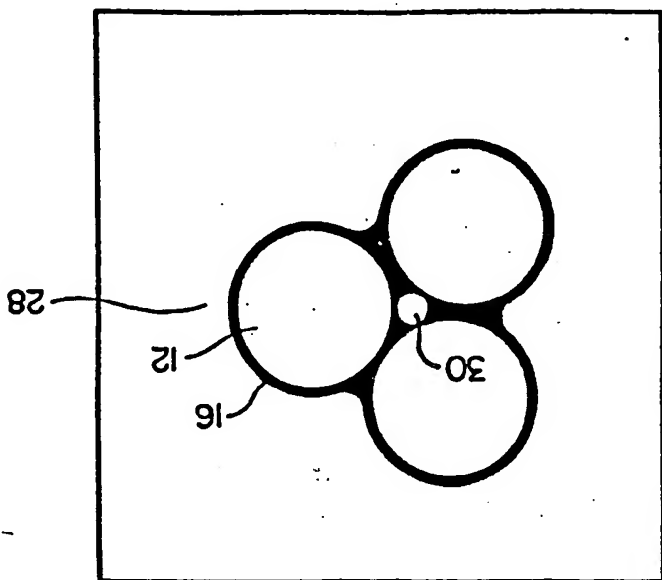


FIG-4

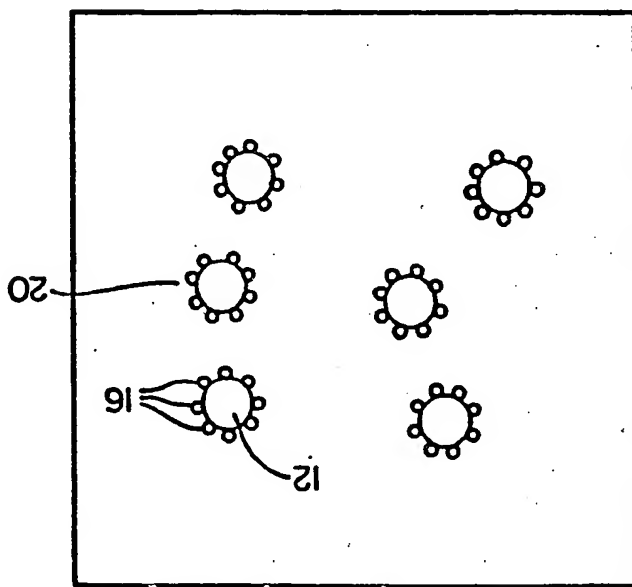


FIG-3

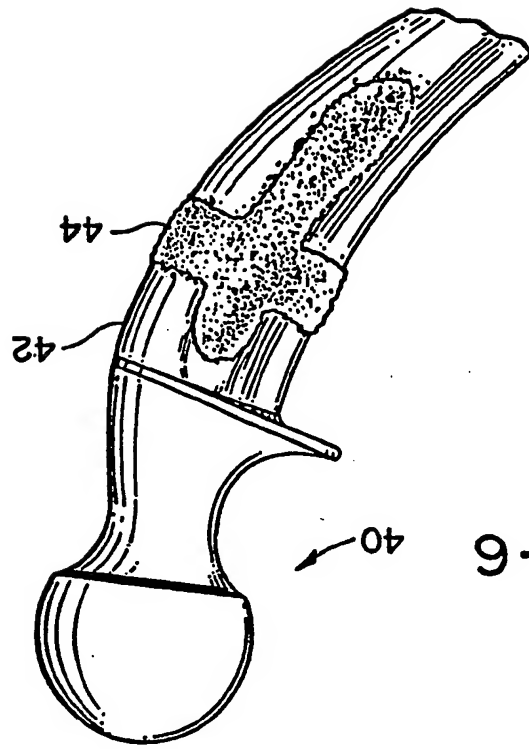


FIG-6

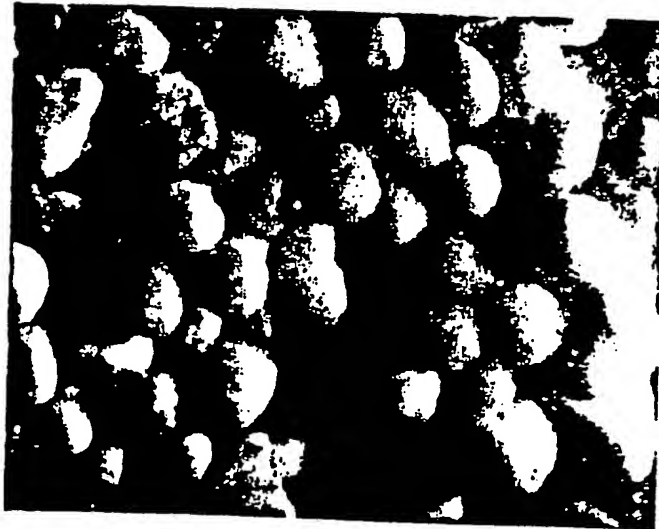


FIG-5

DOCUMENTS CONSIDERED TO BE RELEVANT		DOCUMENTS CONSIDERED TO BE RELEVANT	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	US-A-4 156 943 (J.P. COLLIER) * Claim 1 *	1,8,9,	C 04 B 38/00 A 61 F 2/30 A 61 K 6/06 A 61 L 27/00 C 03 C 4/00
Y	US-A-1 929 425 (E.T. HERMANN) * Claim 1; page 1, lines 92-102; page 2, lines 24-30 *	1,8,9,	
A	WO-A-8 604 807 (UNIVERSITY OF DAYTON) * Abstract *	1,10-12	
A	US-A-4 475 892 (F.R. FAUNCE) * Figure 9; Column 10, lines 34-38; claims 1,14,15 *	1	
A	GB-A- 701 802 (R.W. YOUNG)		
A	DE-A-3 445 711 (K. DRAENER)		
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		24-02-1988	DAELEMANN P.C.A.
CATEGORY OF CITED DOCUMENTS T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : technological background O : non-written disclosure P : intermediate document X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category & : member of the same patent family, corresponding document			

EP 87 31 0161

Application Number

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